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A Study on Development of Pollution Index Models and Multivariate Statistical Analysis for Heavy Metals in the Soils of APIIC, Visakhapatnam

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ABSTRACT

Soil pollution is a worldwide problem caused by both natural and anthropogenic activities. This has resulted in health and physiological problems to both plants and animals. This study investigated heavy metals in soils within the immediate vicinity. Soils from Seven APIIC zones in Visakhapatnam were collected and analysed for physicochemical characteristics and heavy metals. The data obtained were subjected to the pollution index model and multivariate statistical analysis. The data obtained showed that the soils are rich in zinc, and heavy metals are above trace level with a minor positively skewed distribution. The analysis of pollution index, geoaccumulation index and ecological risk factors in soils in all the locations showed that they are mainly contaminated and polluted by Cd followed by Zn. The mean heavy metal concentrations around APIIC can be arranged in increasing order as Cr < Co < Pb < Cu < Cd < Zn. Element pairs such as Zn-Pb, Zn-Cu, Zn-Cd, Pb-Cu, Pb-Cd, Cu-Cr, Cd-Co and Cr-Co showed strong positive correlation coefficient "r" indicating their association in the study area. The observed concentrations of heavy metals revealed that soil contamination has been increasing and measures must be taken to ensure the adoption of more environment-friendly practices.

INTRODUCTION

Heavy metals are released into the environment by both natural and anthropogenic sources. The chemical weathering of minerals; and the anthropogenic sources that are associated with industrial, agricultural, mining, land disposal of waste, waste incineration, etc. are the major sources of these metals (Guerra et al. 2012). The soil contamination by heavy metals due to these activities are becoming a major concern throughout the world. Heavy metals contamination of topsoil has been a major concern for their toxicity, persistence and recalcitrant nature. Toxicity of these compounds has been reported extensively (Momodu & Anyakora 2010, Anyakora et al. 2013). They amass over the time in soils, which act as a sink from which these toxicants are discharged into the groundwater and plants and end up through the food chain causing different toxicological impacts. Impacts of raised concentrations of heavy metals to soil capacities, soil microbial composition and microbial development have for some time been accounted for under both field and laboratory conditions (Tyler et al. 1989). Health effects of elevated levels of Zn are severe vomiting, diarrhoea, bloody urine, liver and kidney failure and anaemia (Fosmire 1990), while excessive Pb causes inhibition of haemoglobin synthesis, dysfunction of the kidneys, reproductive systems and cardiovascular system (Ferner 2001). Other effects of Pb are damage to the gastrointestinal system, mental retardation in children, infertility and abnormalities in pregnancy (Dara 2000). Excess Cd has been reported to bring about renal dysfunction, anaemia, hypertension, bone marrow disorder, cancer, kidney damage, bronchitis, liver and brain disorder (Dara 2000), while, high concentration of manganese could result in kidney failure, liver and pancreases malfunctioning (Underwood 1977). Human activities in urban areas largely contribute to the contamination of urban soils and this is a major health concern. Iwegbu et al. (2006) reported elevated concentration of Cd, Cr, Cu, Pb, Ni, Co and Zn in an automobile mechanic workshop soil while Dauda & Odoh (2012) in their study revealed the high degree of contamination of Pb, Cd and Zn in soil from fuel filling stations in Benue state. In addition, Ubwa et al. (2013) reported high levels of Cd, Zn, Ni, Cr and Pb from the soils around the Gboko area. The extent of human impact is now so pervasive and profound, that there is a need to investigate the levels of heavy metals in soils from different anthropogenically influenced sites. The objective of

this study is to determine the physicochemical characteristics and heavy metals in surface and sub-surface soils from the selected sites in Visakhapatnam.

MATERIALS AND METHODS

Study Area

Visakhapatnam is one of the major port cities on the east coast of India. After bifurcation of Andhra Pradesh state in 2014, this city became its business capital with an area of 550 km². Seven areas were randomly selected as sampling sites in APIIC zone and located using GPS positions (Table 1). The base map (Fig.1) was prepared from these sampling locations.

Sampling and Preparation

Soil samples were taken from depths of 0-15 cm. All the soil samples were stored in clean polythene bags and brought to the laboratory. The soil samples were air-dried, ground and passed through 2 mm sieve for physicochemical and heavy metal analysis.

Physico-Chemical Analysis of Soil Samples

The soil pH and conductivity were determined in 1 (soil):5 (water) suspension using HM digital meter-CO-100 and Equip-Tronics EQ-614 respectively. Soil texture and organic

carbon were determined by the hydrometer method (Jacob & Clark 2002) and Walkley-Black wet oxidation method (Nelson & Sommers 1982) respectively. A factor of 1.72 was multiplied with organic carbon content to determine Soil organic matter.

Heavy Metal Analysis

For heavy metal (Zn, Cr, Cu, Cd, Co and Pb) determination, one gram of soil was digested with 15 mL of aqua regia at 80°C till a transparent solution was obtained (Wen & Allen 1999). The digested samples were filtered and diluted with de-ionized water up to 50 mL and analysed for the metals, viz. zinc (Zn), chromium (Cr), copper (Cu), cadmium (Cd), cobalt (Co) and lead (Pb) by atomic absorption spectrophotometer (AAS).

Pollution Index Model

Contamination factor (C_f): Lacatusu (2000) standards were adopted in the current study for the interpretation of the contamination factor. The factors were used to ascertain the soil contamination levels by heavy metals. The C_f is the ratio of the concentration of heavy metals to the background value. These values are in the range of 1-6.

Contamination factor (C_f) =
$$\frac{C_m}{C_1}$$
 ...(1)

Where, C_m is the concentration of metals and C_b is the background value.

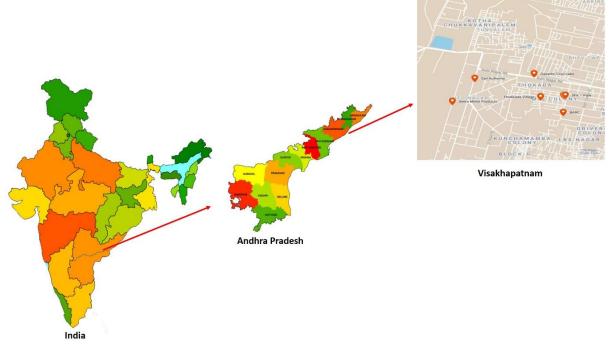


Fig. 1: Location map of the study area.

Table 1: Sampling sites and GPS positions.

S.no	Locations	Name	GPS positions		
1	Seera Metal Products	S1	N 17.695042	E 83.185539	
2	Sail Authority	S2	N 17.698512	E 83.188167	
3	Gayathri Cryo cabs	S3	N 17.699218	E 83.195095	
4	BARC	S4	N 17.693370	E 83.198513	
5	LIG – Park	S5	N 17.695945	E 83.198546	
6	SFA – Park	S6	N 17.695955	E 83.198760	
7	Thokkada Village	S7	N 17.695727	E 83.195859	

The EGASPIN (2002) target values for heavy metals (Table 2) were taken as the background value for the analysis. The range for the significance of intervals of contamination is given in Table 3.

Pollution Index (PI): It is a measure of the degree of overall contamination in a particular location. Tomlinson et al. (1980) procedure was used for calculating the pollution index (PI) for each location as per Equation 2.

Table 2:	Target	values	for	heavy	metals	(mg/kg).
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Metals	Target values (mg/kg)	Intervention values (mg/kg)
Iron (Fe)	38000	-
Zinc (Zn)	140	720
Lead (Pb)	85	530
Cobalt (Co)	20	240
Copper (Cu)	36	190
Chromium (Cr)	100	380
Nickel (Ni)	35	210
Manganese (Mn)	850	-
Arsenic (As)	1.0	10
Cadmium (cd)	0.8	17

Source: EGASPIN, 2002

Table 3: Significance of intervals of contamination factor/pollution index (C_f/PI).

C _f /PI	Significance
< 0.1	Very slight contamination
0.10 - 0.25	Slight contamination
0.26 - 0.5	Moderate contamination
0.51 - 0.75	Severe contamination
0.76 - 1.00	Very severe concentration
1.1 – 2.0	Slight pollution
2.1 - 4.0	Moderate pollution
4.1 - 8.0	Severe pollution
8.1 - 16.0	Very severe pollution
> 16.0	Excessive pollution

Source: Lacatusu (2000)

$$PI = (Cf1 \times C_f2 \times C_f3 \times \dots C_f n)^{1/n} \qquad \dots (2)$$

Where, n is the number of metals and C_f is the contamination factor. The PI is a potential tool that was used to access environmental pollution.

Geo- Accumulation index (Igeo): Muller (1979) formula was used in this study to calculate the index and the values for the various metals are given in Equation 3.

$$I_{geo} = \log_2 (C_n / 1.5 B_n)$$
 ...(3)

Where,

 C_n = Contamination of the heavy metal in the soil.

 B_n = Geochemical background of the element or world average of the element in shale.

Muller proposed seven classes (ranging from 0-6) of the geo-accumulation index to classify the levels of contamination of soils by the metals.

Class $0 = I_{geo} \le 0$ (practically uncontaminated)

Class 1 = $0 \le I_{geo} \le 0$ (uncontaminated to moderately contaminated)

Class 2 =
$$1 \le I_{geo} \le 2$$
 (moderately contaminated)

Class 3 = $2 \le I_{geo} \le 3$ (moderately to heavily contaminated)

Class $4 = 3 \le I_{geo} \le 4$ (heavily contaminated) Class $5 = 4 \le I_{geo} \le 5$ (heavily to extremely contaminated) Class $6 = 5 \le I_{geo} \le 6$ (extremely contaminated)

The values that fall other than 6 of the above classes are considered to be in an open class. In that class, the value of the element is many-folds greater than the background value of the metal (Table 4).

The background value taken is considered from world average value in shale (mg/kg) of the metals determined in the study are Fe = 47200, Zn = 95, Pb = 20, Co = 19, Cu = 45, Cr = 90, Ni = 68, Mn = 850, As = 13 and Cd = 0.3 mg/kg.

Ecological risk factor (\mathbf{E}_r): Hakanson (1980) suggested the ecological risk factor, which is a quantitative expression of potential ecological risk of the given contamination and

Table 4: Toxic response factor for calculation of ecological factor calculation.

Metals	Toxic response factor	
Iron (Fe)	NA	
Zinc (Zn)	1	
Lead (Pb)	5	
Cobalt (Co)	5	
Copper (Cu)	5	
Chromium (Cr)	2	
Nickel (Ni)	5	
Manganese (Mn)	1	
Arsenic (As)	10	
Cadmium (cd)	30	

NA: Not available

is defined as the ratio of the toxic response factor to the contaminant as given in Equation 4.

$$E_r = T_r \times C_f \tag{4}$$

Where, T_r is the toxic response factor for a given contaminant and C_f is the contamination factor. The risk factors are dived into 5 categories.

- $E_r < 40$ (low potential ecological risk)
- 40 $E_r < 80$ (moderate potential ecological risk)
- 80 $E_r < 160$ (considerable potential ecological risk)
- 160 $E_r < 320$ (high potential ecological risk)
- E_r 320 (very high ecological risk)

The aim of the risk factor was originally a diagnostic tool for water pollution control, but currently, we utilized it for accessing the soil quality of a location that is contaminated with heavy metals.

Statistical Analysis

The analysis of physicochemical characteristics and heavy metal content of soil and plant samples was done in triplicates and the data are presented as mean \pm standard error.

Table 5: Physico-chemical properties of soils.

Statistical analysis was done with the help of Microsoft excel computer software programs.

RESULTS AND DISCUSSION

Soil Physicochemical Properties

The physicochemical properties of soils are given in Table 5. The studied soil is slightly (S5, S6) and moderately alkaline (S1, S2, S3, S4, S7). The pH of the soil is in a range of 7.7-8.26. Soil electrical conductivity, which is a major indicator of salinity of the soil, was found to be low (45-135 mS/cm).

The Soil Organic Matter (SOM) which is the storehouse of plant nutrients and mineral recycling (Rattan et al. 2005) was found to be low (0.296-1.37 %) which can be attributed to the sandy texture of the soil.

Heavy Metal Analysis

Table 5 represents the contents of heavy metals (Zn, Cr, Cu, Cd, Co and Pb) studied in the soils. The Zn, Cr, Cu and Co are required for plants for metabolic activities (Jolly et al. 2013). They ranged from 10.8 to 227.9, 0.01 to 41.4, 1.9 to 78.9 and 10.5 to 20.8 mg/kg respectively. Cd and Pb, which are known toxins and carcinogens (Rajaganapathy et al. 2011), ranged from 24.5 to 71.5 and 0.79 to 51.8 mg/kg. Although extensive use of agrochemicals is prevalent in Visakhapatnam posing a severe risk of heavy metal contamination of soil, the levels of heavy metals in studied soils were below the various maximum permissible limits (Table 6 & 7). This might be due to leaching of metals to lower soil layers, due to the sandy texture of soil and precipitation. The soil heavy metal contents observed in the present study were at similar levels to the heavy metals observed in soil by Dheri et al. (2007).

Pollution Index Model

Zn: PI/C_f values vary from 0.07 to 1.63 in different samples. Sample S7 shows very slight contamination whereas samples S3 and S4 show slight pollution and the remaining samples

Sample	рН	Electrical conductance (mmhos)	Organic carbon %	Zn mg/kg	Pb mg/kg	Cu mg/kg	Cd mg/kg	Cr mg/kg	Co mg/kg
1	8.26	124	0.558	68.7	20.9	78.9	36.6	36.4	10.5
2	8.05	98.7	0.93	34.1	8.3	22.1	41.7	41.4	20.8
3	8.23	79	0.679	227.9	4.8	23.7	33.8	10.2	15.3
4	7.94	138	1.37	152.3	51.8	48.9	71.5	10.9	15.1
5	7.7	87	1.051	103.9	43.8	9.2	89	5.33	15.6
6	7.74	45	0.456	35.4	5.8	7.19	50.5	0.01	20.6
7	8.22	61.8	0.296	10.84	0.79	1.9	24.5	2.58	10.9

Metal	Station 1	Station 2	Station 3	Station 4	Station 5	Station 6	Station 7
Zn	0.490714	0.243571	1.627857	1.087857	0.742143	0.252857	0.077429
Pb	0.245882	0.097647	0.056471	0.609412	0.515294	0.068235	0.009294
Cu	2.191667	0.613889	0.658333	1.358333	0.255556	0.199722	0.052778
Cd	45.75	52.125	42.25	89.375	111.25	63.125	30.625
Cr	0.364	0.414	0.102	0.109	0.0533	0.0001	0.0258
Co	0.525	1.04	0.765	0.755	0.78	1.03	0.545

Table 6: Contamination Factor/pollution Index for heavy metals for various stations.

Table 7: Geoaccumulation index at different stations.

Matal	Station 1	Station 2	Station 2	Station 4	Station 5	Station (Station 7
Metal	Station 1	Station 2	Station 3	Station 4	Station 5	Station 6	Station 7
Zn	0.145114	0.072029	0.481389	0.3217	0.219466	0.074775	0.022897
Pb	0.209697	0.083277	0.04816	0.519727	0.43946	0.058193	0.007926
Cu	0.351836	0.09855	0.105684	0.218058	0.041025	0.032062	0.008473
Cd	24.48133	27.89267	22.60844	47.82556	59.53111	33.77889	16.38778
Cr	0.081159	0.092307	0.022742	0.024303	0.011884	2.23E-05	0.005752
Co	0.110895	0.219677	0.161589	0.159477	0.164758	0.217565	0.115119

show moderate contamination. Geoaccumulation index of Zn in all samples indicates that soil has moderate contamination. An ecological risk factor is very low in all samples.

Pb: PI values vary between 0.01 and 0.52. Severe contamination to soil happened by Pb in samples S4 and S5. Negligible distribution occurred in sample S7. According to geoaccumulation index, the soil is not exclusively contaminated by Pb in all samples. Ecological risk factor through Pb is low in all samples.

Cu: Contamination factor varies from 0.05 to 2.19. Moderate pollution is caused by Cu in sample S1, and slight pollution observed in sample S4. Soils in all the stations show moderate contamination by Cu. Low potential risk factor observed for all soils.

Cd: Excessive pollution is caused by Cd in all stations. The PI values vary from 30 to 89. These high values are due to welding operated small-scale engineering workshops located near the stations. Geoaccumulation index suggests that soils in all the locations are extremely contaminated by Cd. Ecological risk factor values exist in terms of thousands. It clearly shows that these soils are in very high ecological risk. These soils are not at all suitable for cultivation as well as a living.

Cr: Pollution index suggests that soils are contaminated from slight to the severe condition in observed locations. Geoaccumulation index also suggests that soils in all locations are uncontaminated by Cr. Ecological risk factor is negligible in case of Cr.

Co: Pollution index values vary from 0.5 to 1.04. Severe

contamination of soil was observed by cobalt in all locations, particularly in samples S2 and S6. Geoaccumulation index shows moderate contamination by Co to soils in all samples. Low potential toxic response factor was observed in all locations.

Statistical Analysis

The standard statistical analysis (mean, standard deviation, skewness, kurtosis) carried out to describe the physicochemical characteristics and heavy metals contents in the soil is presented in Tables 8 and 9.

Effect of pH: As per the US Department of Agriculture (USDA 1993), samples S5 and S6 are slightly alkaline and samples S1, S2, S3, S4 and S7 are moderately alkaline. Positive correlation was obtained for pH with EC (r = 0.22), Zn (r = 0.11), Cu (r = 0.41) and Cr (r = 0.43). Higher pH value indicates a low value of organic carbon (McIntosh & Allen 1993). This is clear when observing samples S1 and S4.

Effect of electrical conductance (EC): EC values vary between 45 mmhos and 138 mmhos. Higher value was observed in the sample S4 and lower value in sample S6. Higher EC values indicate the availability of various salts in the soil and also shows that leaching of soil leads to contamination of groundwater. The positive correlation was obtained with all parameters except Co (r = -0.29), which indicates that EC is interdependent on all parameters except cobalt.

Effect of organic carbon (OC): OC varies in the range of 0.291.37%. Sample S4 has a higher OC value of 1.37%, whereas sample S7 has a lower value of 0.29%. The data in

Table 8: Statistical analysis.

	pН	EC mmhos	OC %	Zn mg/kg	Pb mg/kg	Cu mg/kg	Cd mg/kg	Cr mg/kg	Co mg/kg
Minimum	7.7	45	0.296	10.84	0.79	1.9	24.5	0.01	10.5
Maximum	8.26	138	1.37	227.9	51.8	78.9	89	41.4	20.8
Median	8.05	87	0.679	68.7	8.3	22.1	41.7	10.2	15.3
Mean	8.02	90.5	0.763	90.45	19.46	27.41	49.66	15.26	15.54
Standard deviation	0.2344	32.87	0.374	77.37	20.44	27.53	22.89	16.67	4.092
Skewness	-0.4367	0.170	0.501	0.995	0.943	1.290	0.947	1.035	0.157
Kurtosis	-1.764	-0.87	-0.61	0.217	-0.98	1.056	-0.09	-0.82	-1.19
Standard error	0.2333	1.754	2.272	2.262	2.355	1.505	2.348	1.144	2.365
Standard error of mean	0.0886	12.42	0.142	29.25	7.738	10.40	8.652	6.299	1.547
Variance	0.0550	1081	0.140	5986	419.2	757.7	524.0	277.8	16.74
Coefficience of variation	2.9233	36.33	49.07	85.54	105.2	100.4	46.10	109.2	26.33

Table 9: Correlation matrix for soil parameters.

Correlation	рН	EC mmhos	OC %	Zn mg/kg	Pb mg/kg	Cu mg/kg	Cd mg/kg	Cr mg/kg	Co mg/kg
pН	1.0000	0.2204	-0.3988	0.1120	-0.4636	0.4155	-0.8170	0.4289	-0.5961
EC mmhos	0.2204	1.0000	0.6862	0.3217	0.6769	0.8216	0.2798	0.5677	-0.2988
OC %	-0.3988	0.6862	1.0000	0.4546	0.8400	0.2392	0.7539	0.1484	0.2498
Zn mg/kg	0.1120	0.3217	0.4546	1.0000	0.3313	0.2268	0.2249	-0.1528	-0.0818
Pb mg/kg	-0.4636	0.3217	0.8400	0.3313	1.0000	0.3525	0.8623	-0.0609	-0.1148
Cu mg/kg	0.4155	0.8216	0.2392	0.2268	0.3525	1.0000	-0.0512	0.6130	-0.4159
Cd mg/kg	-0.8170	0.2798	0.7539	0.2249	0.8623	-0.0512	1.0000	-0.2549	0.2518
Cr mg/kg	0.4289	0.5677	0.1484	-0.1528	-0.0609	0.6130	-0.2549	1.0000	0.0370
Co mg/kg	-0.5961	-0.2988	0.2498	-0.0818	-0.1148	-0.4159	0.2518	0.0370	1.0000

Table 8 clearly indicate that organic carbon is strongly interdependent on Pb (r = 0.84) and Cd (r = 0.75) and moderately correlate with Zn (r = 0.45), Cu (r = 0.24) and Co (r = 0.25), whereas weakly interdependent on Cr (r = 0.15). A negative correlation was observed with pH (r = -0.39) which shows that organic carbon oppositely dependent on pH.

Analysis of Heavy Metals

Effect of Zn: Amount of Zn present in given samples varies between 10.84 mg/kg and 227.9 mg/kg. Sample S7 has lower value of 10.84 mg/kg and sample S3 a higher value of 227.9 mg/kg. The positive correlation obtained with all parameters except Cr and Co even though the correlation is weakly interdependent on pH, EC, OC, Pb, Cd and Cu

Effect of Pb: Amount of Pb present in given samples varies from 0.79 mg/kg to 51.8 mg/kg. In sample S7 have lowest value (0.79 mg/kg) whereas sample S4 contains the highest value of 51.8 mg/kg. A positive correlation was observed with EC, OC, Zn, Cu and Cd whereas a negative correlation with Cr and Co. Among EC, OC, Zn, Cu and Cd, OC is strongly

correlated with Pb (r = 0.84). In the study areas, due to the presence of automobile service centres fuel effluent wastage with Pb and organic carbon enters into the soil. In fuels, Pb and Cd are added as anti-knocking agents hence there is a strong correlation between Pb and organic carbon.

Effect of Cu: Amount of Cu present in given the samples varies from 1.90 mg/kg to 48.9 mg/kg. 1.90 mg/kg is the lowest value in sample S7, and 48.9 mg/kg be the highest value in sample S4. Positive correlations were observed with EC, OC, Zn, Pb and Cr, and weak negative correlation with Cd (r = -0.05) and a strong negative correlation with Co (r = 0.41).

Effect of Cd: Amount of Cd lies between 24.5 mg/kg and 71.5 mg/kg. Sample S4 gets a higher value (71.5 mg/kg), and sample S7 a lower value (24.5 mg/kg). The positive correlation was obtained with EC, OC, Zn, Pb and Co whereas a negative correlation with pH and Cr.

Effect of Cr: Chromium ranges from 0.01mg/kg to 41.4 mg/kg. Sample S6 has a least value of 0.01 mg/kg,

and sample S2 the highest value. The positive correlation obtained with pH, EC, OC and Cu but a negative correlation with Zn, Pb and Cd whereas no correlation with Co.

Effect of Co: The values of cobalt in samples vary between 10.5 mg/kg and 20.8 mg/kg. Sample S1 has a lower value of 10.5 mg/kg, and sample S6 a higher value (20.6 mg/kg). A slight positive correlation was observed with OC and a partial negative correlation with all parameters except Cr and no correlation with Cr. Abundance of Co in the soil acts as an inhibitor for soil biological activity (Zaborowska et al. 2016).

CONCLUSION

It can be thus concluded from the present study that the studied soil samples were slightly-moderately alkaline with moderate SOM. The heavy metal content in the soil is above the trace levels despite intensive anthropogenic practices which can be due to the sandy texture of soil and leaching of metals to lower ground layers. From the analysis of PI, geoaccumulation index and ecological risk factors, soils in all the locations are mainly contaminated and polluted by Cd followed by Cu and Zn. The remaining metals moderately influence soil pollution. Major soil pollution control precautions should be taken in stations 4, 5 and 6. Station 7 observed moderate soil contamination of all metals. Multivariate statistical methods applied in this study proved useful in the characterization of heavy metals sources in soils form APIIC zone. Zinc showed excessively high concentrations in the study area. The increasing orders of heavy metals in soils are Cr, Co, Pb, Cu, Cd and Zn. Element pairs such as Zn-Pb, Zn-Cu, Zn-Cd, Pb-Cu, Pb-Cd, Cu-Cr, Cd-Co and Cr-Co showed strong positive correlation indicating their association in the study area. Therefore, measures must be taken to ensure the adoption of more environmentally friendly practices.

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